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Relationship between CO, POHC, and PIC Emissions from a Simulated Hazardous Waste Incinerator

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On the Relationship Between CO, POHC, and PIC Emissions from a Simulated Hazardous Waste Incinerator

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Measurements conducted on full-scale hazardous waste incinerators have occasionally shown a relationship between carbon monoxide (CO) emissions and emissions of toxic organic compounds. In this study, four mixtures of chlorinated C_1 and C_2 hydrocarbons were diluted in commercial-grade heptane and burned in a water-cooled turbulent flame reactor (TFR) under two different excess air levels. No correlation between CO and organic emissions could be discerned. Reasons for this lack of observable correlations are discussed in terms of combustion and chemical reaction kinetic theory.

There is increasing regulatory and public concern for the need to continuously monitor the performance of hazardous waste incineration systems.[1] Even though incineration systems may initially comply with the current regulatory requirements during a trial burn, it has been recognized that transient "failures" of the incinerator may occur. These can potentially result in increased emissions of residual toxic components of the waste feed, principle organic hazardous constituents (POHCs) and/or combustion by-products, products of incomplete combustion (PICs). Continuous measurement of carbon monoxide (CO) has been suggested as a suitable means by which to constantly measure incinerator performance. It is easy to measure and is universally present as a relatively stable combustion by-product.

If CO is to be useful as a continuous indicator of incinerator performance, differences in CO emissions must be shown to, in some way, reflect differences in emissions that occur as a result of changes in incinerator operating conditions. Ideally, this relationship should be one which would allow for the determination of an "action level" for CO above which steps would need to be taken to prevent stack emissions of toxic materials. The incinerator could be operated below the predetermined CO "action level" without emitting toxic materials from its stack.

In this study, the feasibility of CO as a performance surrogate was investigated by comparing CO emissions with the emissions of residual POHCs and PICs from the combustion of mixtures of chlorocarbons of varying elemental and molecular composition. This work was performed on a pilot-scale turbulent flame reactor (TFR) under both oxidative and near-stoichiometric operating conditions.

This paper begins with a description of the experiments conducted in carrying out this study. Following that, a discussion of the results obtained is presented.

Experimental Equipment and Design

The TFR's design both limits the experimental data that can be obtained and expands the number of combustion related phenomena that can be studied at any one time.

Figure 1 shows the turbulent flame reactor (TFR). It is a 150,000 (BTU/hr) water-jacketed stainless steel combustion device. A mixture of commercial grade heptane and the chemical compounds to be studied are introduced into the reactor through a Delavan pressure atomizing nozzle at approximately one gallon per hour.

Angular momentum is imparted to the incoming combustion air stream through the use of an adjustable vane wind box which diverts part of the incoming air stream into a swirling pattern. Swirl numbers of 0 to 2.76 resulting in a variety of flame patterns can be produced with this device.

All process measurements are made at the outlet of the TFR. Exhaust gas temperature is measured using a Type K (chromel/alumel), thermocouple. Levels of CO and CO_2 are measured with nondispersive infrared continuous gas monitors. Oxygen levels are continuously measured using a paramagnetic monitor.

Measurement of volatile POHCs and PICs are performed using a modified volatile organic sampling train (VOST). Figure 2 shows the sampling system used. It consists of a gas conditioning system to dry and cool the sample gases, a sample trap containing 0.25 grams of Tenax-GC resin, two rotameters and a dry gas meter for measuring the exhaust gas flowrate. Its chief limitation is that only compounds with boiling points up to 150 C° can be sampled and adequately quantified. Further descriptions of the TFR can be found in the literature.[2-4]

Unlike other more controllable experimental combustion devices, the TFR is limited in both the degree to which experimental conditions can be controlled and the degree to which the conditions within the TFR can even be measured. For example, the oxygen level measured at the outlet of the TFR provides an indication of the average oxygen concentration existing at that point. Visual observation suggests that the oxygen concentrations are much lower in the flame zone which is located upstream of the sampling ports. Even when the oxygen concentration observed at the outlet indicates that more than enough oxygen is present within the TFR, soot formation rapidly coated the TFR's viewports making visual access impossible. This suggests that pyrolysis processes were taking place on a significant scale even though measurements of oxygen content in the exhaust indi-

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cated an oxidative environment. Since our only measurement access was at the exhaust, we were unable to make measurements within the TFR that would have enabled us to determine the extent of these oxygen deficient zones where the pyrolysis processes were apparently taking place. So, even though we set out to establish an oxidative environment within the TFR, we were unable to eliminate pyrolytic zones. Further, we were unable to make any measurements in the pyrolytic zones that were invariably created and which played a significant role in determining the emissions from the TFR.

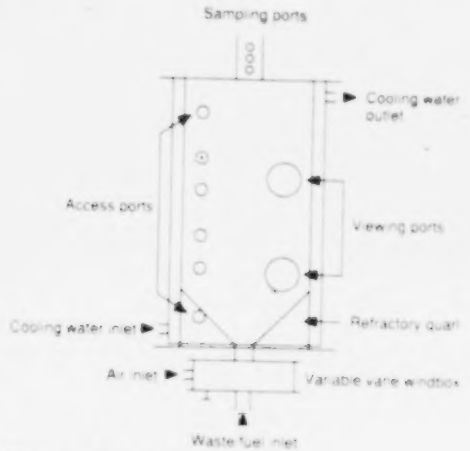

Figure 1. Turbulent flame reactor.

These nonuniformities also occur in full scale combustion devices. If these nonuniformities are significant in determining the emissions from the TFR, then the CO levels detected in the exhaust must, in some way, correlate with these emissions.

Another difference between the TFR and other small experimental combustion devices is that several interdependent phenomena affect the operation of the TFR. Not only are pyrolysis reactions occurring simultaneously with oxidative reactions, but mass and heat transfer affect the reactions that are taking place. As mentioned above, oxygen deficiencies caused by inefficient air/fuel mixing lead to significant pyrolysis even under "oxidative" conditions. Attempts to counteract this effect by increasing the swirl induced in the combustion gases results in significant post-flame cooling which changes the emissions observed. This is illustrated by the following visual observation.

At low swirl numbers, the flame produced was long, almost running the length of the TFR. Exhaust temperatures measured at these conditions were high. CO levels were relatively low. At higher swirl numbers, the flame produced was much more compact, occupying only one third of the TFR's volume. Exhaust temperatures were lower and CO levels were somewhat higher under these conditions. Although it is conceivable that flame temperatures were higher in this case because of more efficient air/fuel mixing, exhaust temperatures were lower. This suggests that the combustion gases were cooled to a much greater extent in the post-flame zone in this case. One explanation for this is that, at higher swirl numbers, the angular momentum imparted to the incoming combustion gases caused them to hug the water-cooled walls of the TFR as they spiraled downstream of the flame zone towards the exhaust duct. The extended contact with the cold walls cooled the gases more extensively.

The differences in CO level and temperature observed with changes in swirl number suggest that the heat transfer resulting from enhanced contact with the water-cooled walls which occurs at higher swirl numbers significantly affects the composition of the exhaust gases. It is likely, however, that the exhaust gases in a small layer immediately adjacent to the water-cooled walls were dramatically affected by the heat transfer. This suggests that reactions which occur in the

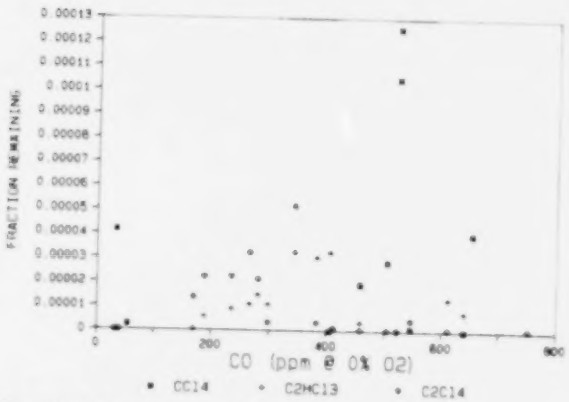

Figure 3. CO concentration vs. POHC fraction remaining.

thermal boundary layer of the post-flame zone are significant and may affect the type and amount of trace organic emissions observed in exhaust from combustion devices. Since the thermal boundary layer is relatively small, the volume of exhaust gases responsible for the emissions under these conditions is very small.

The experiments conducted in this study involved burning four different mixtures of chlorinated C_1 hydrocarbons and C_2 hydrocarbons diluted with commercial-grade heptane under two different levels of excess air (see Table I). The temperatures, oxygen and carbon monoxide levels indicated are target values around which the actual values fluctuated during the tests. The chlorinated components were selected because their high temperature decomposition properties have been studied by other researchers and are relatively well understood.[3-8]

The experiments involved the following procedure. Experimental conditions were established and the TFR was allowed to equilibrate while burning heptane only. Heptane spiked with the compounds of interest was then introduced and the system allowed to once again equilibrate. After equilibration, sampling began. This involved taking three samples in rapid succession without making any changes in the TFR's intended operating conditions. The experiment took between three and four hours to complete. During that

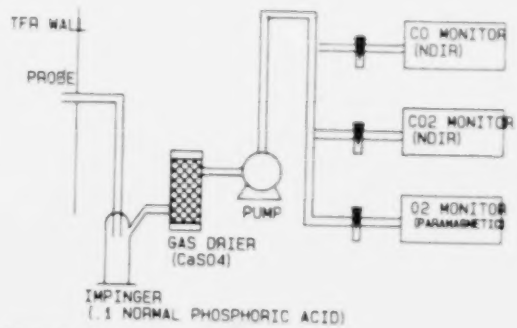

Figure 2. Continuous monitors.

Table I. Experimental test mixtures and test conditions

Mixture	Component	Mass (g)	Cl/H (excluding heptane)	Test	Exhaust O_2 (%)	Average Exhaust T (°F)	Exhaust[a] CO (ppm)
1A	CH_2Cl_2	5.682	6.4	1	6.0–6.3	930	550
	$CHCl_3$	78.47					
	CCl_4	113.642		3	4.0	888	80
	C_7H_{16}	2500					
1B	CH_2Cl_2	55.05	2.0	2	6.0–6.3	930	550
	$CHCl_3$	118.0					
	CCl_4	11.8		4	4.0	888	80
	C_7H_{16}	2500					
2A	$C_2H_2Cl_4$	8.311	6.4	5	6.6–6.8	940	450
	C_2HCl_3	83.5					
	C_2Cl_4	107.7		7	3.5	910	200
	C_7H_{16}	2500					
2B	$C_2H_2Cl_4$	7.8816	12.5	6	6.6–6.8	940	450
	C_2HCl_3	39.01					
	C_2Cl_4	157.63		8	3.5	910	200
	C_7H_{16}	2500					

[a] Average value during test.

time, stripchart recordings were made of the exhaust gas concentrations measured by the continuous emission monitors. This process was repeated eight times to allow for the collection of data on each of the four mixtures under two different sets of operating conditions.

The TFR operated at the fuel-rich and fuel-lean limits of flame stability due to the chosen operating conditions. These conditions were suboptimal and were chosen so that relatively easily measurable levels of organic emissions were produced.

Results

The results are summarized in Figures 3 and 4 which show the fraction remaining for both POHC and PIC plotted against the average level of CO emissions observed during the sampling period. The results indicate the following:

- No correlation was observable between CO concentration and exhaust temperature or oxygen concentration. Table II shows the correlation coefficients calculated between each of the organic compounds observed in the exhaust and the CO, and O_2 levels, and the exhaust temperature. The correlation coefficients calculated between the CO levels observed and the emission levels of the organic chemicals observed in the exhaust were too low to suggest a relationship.
- As indicated in Figure 3, there was no observable correlation between CO stack emissions and organic fraction emissions (i.e., the fraction of POHC which was undestroyed or the mass emissions of PICs). Note that destruction efficiency (DE) is related to the fraction of POHC remaining (fr) by the expression DE = 100*(1-fr). Figure 4 presents a plot of CO concentration versus measureable PIC emissions (C_6H_6 and C_6H_5Cl) where the mass emission rate of PICs has been normalized to the total mass feed rate of the chlorinated compounds in the test mixture.
- High CO emissions were not always accompanied by the same organic emissions. When tests were run at high excess air (tests 1, 2, 5, 6), the high CO levels observed were accompanied by high levels of residual chloromethanes and ethylenes for mixtures 1A/1B and 2A/2B, respectively. Conversely, at low excess air (tests 3, 4, 7, 8), the high CO levels observed were accompanied by emissions of benzene, soot, and trichloroethylene. Figures 5 and 6 illustrate this observation.

Discussion

In trying to understand why a correlation between CO and volatile organic emissions was not observed in this study, three questions need to be addressed. These include the following:

- If a correlation had existed, could it have been detected using the measurements and techniques employed in this study?

Table II. Correlation coefficients between exhaust temperature, oxygen, carbon monoxide levels and hydrocarbon fraction remaining[a]

	CCl_4	C_6H_6	C_7H_{16}	C_6H_5Cl	C_2HCl_3	C_2Cl_4	CO	Exh. Temp.
C_6H_6	−0.269							
C_7H_6	0.364	−0.193						
C_6H_5Cl	0.561	−0.241	0.050					
C_2HCl_3	−0.121	−0.025	−0.400	−0.264				
C_2Cl_4	−0.022	−0.157	−0.224	0.258	0.368			
CO	−0.248	0.339	−0.052	−0.414	−0.250	−0.484		
Exh. Temp.	0.452	−0.109	0.408	0.125	0.121	0.026	−0.352	
O_2	−0.179	0.268	0.585	−0.291	−0.030	−0.000	−0.075	0.262

[a] Calculated from logarithms of the above quantities.
$y = ax^b + C$ (assuming C is zero).
$\log = b \log(x) + \log(a)$

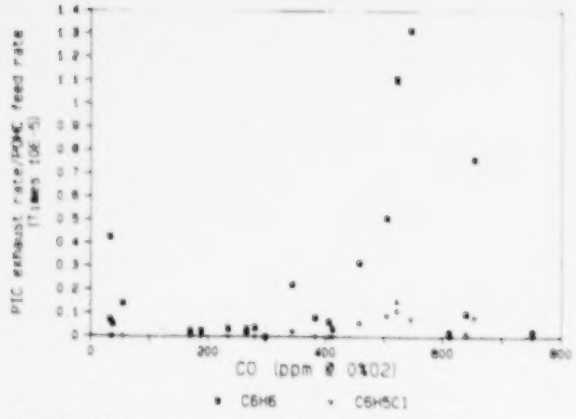

Figure 4. CO concentration vs. normalized PIC emission rate.

- Is there a physical or chemical basis for assuming that CO would accurately trace the formation and emission of volatile organic emissions?
- How can the results observed in this study be reconciled with the results of other studies that support the existence of a CO/organic emission correlation?

Each of these questions will be addressed below.

Could the measurements adequately detect a correlation? Carbon monoxide levels observed when making a gross measurement of the exhaust gas composition at the outlet of the TFR may be too insensitive to detect the formation of trace quantities of organic emissions. In this study, CO was measured in parts per million (ppm) while the organic emissions were in parts per billion (ppb) which is one thousand times as dilute. Minor localized fluctuations in temperature and oxygen concentration may be responsible for the elevated levels of organic emissions observed at the exhaust. These fluctuations may be too small and localized to be detected at the exhaust of the TFR where temperature and CO levels are measured. This concept of localized fluctuations being responsible for observed POHC, PIC, and CO emissions is supported by data presented in Table II. There is a lack of correlation observed for POHC DE, PIC emissions, or CO emissions with operating parameters such as exhaust temperature or exhaust oxygen concentrations.

Aside from differences in sensitivity between the CO measurements and the measurements of organic emissions, there is a fundamental difference between how the two measurements are made. CO is continuously measured throughout the test. Stripcharts from the CO monitor provide a record of instantaneous measurements of CO readings. The CO levels fluctuate. Figure 7 is a sample of the stripchart recordings from one of the tests. Tenax GC samples of the volatile organic chemicals in the exhaust are extractive in nature and provide what is essentially an average concentration over the sampling period. To compare the two measurements, it is necessary to condense the CO data into some kind of average value over the Tenax GC sampling period. There are several ways to do this.

The CO readings could simply be averaged over that period. This has the disadvantage that a simple average CO reading negates the effect of process upsets. Figure 8 is a conceptual illustration of how this could happen. For example, if over a 10 minute sampling period the CO level fluctuates around a very low value (say 10 ppm) and then suddenly increases to 800 ppm for 15 seconds, an average CO level of approximately 30 ppm is obtained when CO readings at 5 second intervals are averaged. The 800 ppm CO spike may have been responsible for much of the emissions observed during that sampling period, yet the average CO value obtained does not reflect the fact that a spike occurred at all. If CO readings are averaged over longer intervals, the 800 ppm spike (and POHC/PIC surges) could be missed entirely.

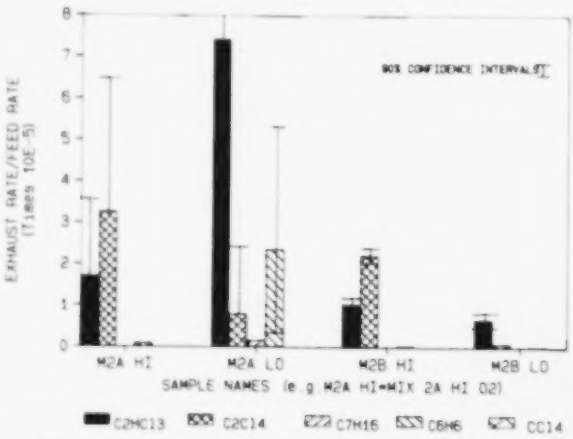

Figure 8. Average fraction remaining chlorinated C_2s.

Carbon monoxide readings could be averaged in such a way as to give heavier weight to spikes. Then, however, a consistent way of comparing carbon monoxide readings from test to test would have to be developed. For example, a determination would have to be made as to whether one large CO spike was equivalent to three smaller CO spikes. As with other schemes, this one would have to be shown to correlate with organic emissions.

Because of these unanswered questions concerning the measurements of both the CO and volatile organic levels in the exhaust gases, more study is needed before a conclusive determination can be made as to whether there is any "relationship" between CO and POHC or PIC emissions that can be used as an indicator of incinerator performance. However, the following question must also be considered.

Is there a physical or chemical basis for assuming that CO emissions would be related to volatile organic emissions? Generally speaking, the combustion of hydrocarbons proceeds through a sequence of elementary reaction steps to the formation of the thermodynamically stable end products, CO_2 and water. When chlorinated materials are considered, HCl and Cl_2 must be considered thermodynamic end products, depending upon the H to Cl ratio in the reactants.

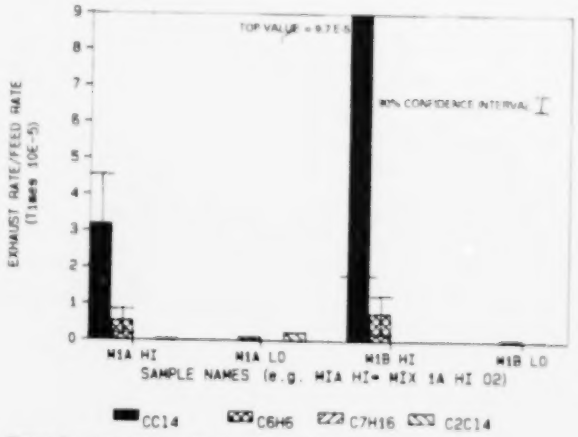

Figure 5. Average fraction remaining chloromethanes.

In reality, combustion reactions occur via free radical chain reactions which include many individual steps. For example, one mechanism for the combustion of propane contains 83 separate reactions. Even though the overall reaction for propane combustion is:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \quad (1)$$

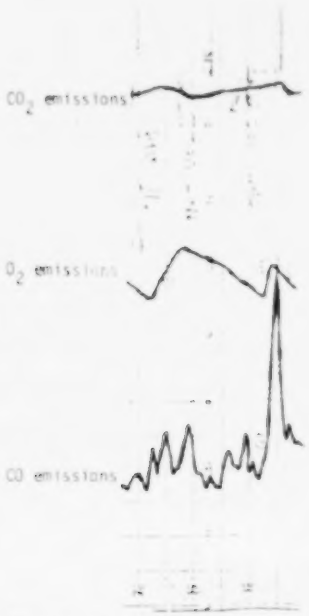

Figure 7. Sample of stripchart recording taken during Tenax sampling for organic emissions. Emission levels of CO and CO_2 are determined by reference to calibration curves and are of different scales. So is the O_2 recording.

Clearly there are many elementary reactions that contribute to this overall result.[9] Not all of these reactions occur in series. Some occur in parallel. Instead of:

$$A \rightarrow B \rightarrow C \quad (2)$$

either:

$$A \rightarrow B \quad (3)$$

or:

$$A \rightarrow C \quad (4)$$

Whether A forms B or C depends on reaction conditions such as temperature and the type and level of free radicals present in the reaction mixture. In addition to the desired thermodynamically stable end products mentioned above, other stable side products are possible from some of the reactions within the overall mechanism. Conditions within the combustor such as temperature and oxygen content affect the relative amounts of side product formed by affecting the relative concentrations of the free radicals which drive the chain reaction's many individual steps. It is generally assumed that the combustion of organic compounds proceeds rapidly to the formation of CO, with the subsequent oxidation to CO_2 being the slowest rate-determining step in the reaction sequence.[10] While most of the feed may react via the predominant pathway outlined above, trace amounts of side products will form as the result of localized deficiencies in oxygen or temperature. Carbon monoxide formation may be the slowest step in the predominant reaction pathway, but is this also the case for the side reactions which may not involve CO? For example, the thermal boundary layer along the water cooled walls of the TFR which was discussed earlier may be responsible for the formation of many of the trace organics observed in the exhaust. Although the gases occupying the thermal boundary layer may account for only a small fraction of the total volume of the TFR's exhaust gases, they may be responsible for the majority of organic emissions observed.

The most likely reaction of CO which can result in the formation of ground state CO_2 is oxygen atom transfer involving the hydroxyl radical (OH)[10,11]

$$CO + OH \xrightarrow{k_{(5)}} CO_2 + H \quad (5)$$

It is well documented through numerous pseudo-equilibrium and kinetic calculations that OH is only present in significant concentrations in systems which contain stoichiometric or excess amounts of molecular oxygen.[11] Thus, the conversion of CO to CO_2 can only occur in an oxidative environment and proceeds by an oxidative pathway which is defined as one that involves the transfer of an oxygenated species.

The rate of *formation* of CO is, in general, a complex function of many elementary reactions and may be expressed in the general form:

$$\frac{d[CO]}{dt} = f(k_1 \ldots k_n)[POHC_1] \ldots [POHC_n][PIC_1] \ldots [PIC_n][Fuel][R_1] \ldots [R_n] \quad (6)$$

where [CO], $[POHC_1] \ldots [POHC_n]$ and [Fuel] are the concentrations of carbon monoxide, all POHCs and the fuel at time t; $k_1 \ldots k_n$ are the rate constants of reaction steps involved in the conversion of the POHC and fuel to CO; $[PIC_1] \ldots [PIC_n]$ are the concentrations of all stable intermediates involved in the reaction sequence; $[R_1] \ldots [R_n]$ are the concentration of all reactive atoms and radicals involved in this sequence. If the rate determining step in the dominant pathway to CO formation could be identified, then expressions could be simplified to include only the reaction parameters up to and including the rate determining step. For a very simple example of the rate limiting step being the pyrolytic unimolecular formation of an intermediate PIC

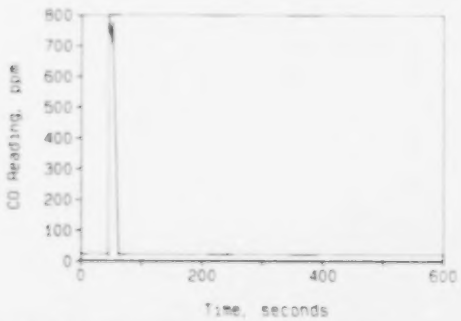

Figure 8. Conceptual illustration of a process upset.

(such as C_2HCl_3 formation from $C_2H_2Cl_4$ via HCl elimination), it can be shown that the rate of CO formation is given by:

$$\frac{d[CO]}{dt} = k_n[PIC_n] = k_1[POHC] \quad (7)$$

when the steady state approximation is invoked for intermediate PICs.

In the most general sense, the CO concentration as a function of reaction parameter (i.e., time, temperature, etc.) de-

pends upon both its rate of formation by the reaction sequence given by $f(k_1 \ldots k_n, [PIC_1] \ldots [PIC_n], [R_1] \ldots [R_n])$, and on its rate of destruction given by $k_{co}[CO][OH]$. Assuming the CO concentration reaches a steady state and equating the formation and destruction rates of CO, the following expression is yielded:

$$[CO] = \frac{k_n}{k} \frac{[PIC_n]}{[OH]} = k_1 \frac{[POHC]}{k} [OH] \quad (8)$$

Since the OH concentration is not constant, CO concentration (emissions) will not be predictably correlated with POHC or PIC levels as operating conditions and OH concentrations fluctuate. We have previously argued that the formation of CO may, in some instances, be delayed for large complex organic molecules such that the CO concentration may be either decreasing or increasing as the POHC or PIC concentration decreases.[12]

In separate studies, we have also presented data that strongly suggests that residual POHC and PIC emissions from hazardous waste incinerators are primarily due to pyrolysis, not oxidative, pathways in oxygen-deficient pockets of the incinerator.[13,14] This hypothesis was set forth based on the observation of primarily "pyrolysis" products from nominally oxygen-rich systems and consideration of the rates of oxidation and pyrolysis of toxic organics obtained from laboratory tests and theory.[3,13-16] These latter considerations suggest that low temperatures (<800°C) are necessary before fast, oxidative pathways can result in observable POHC or PIC emissions. Thus, one may draw the conclusion that pyrolysis pathways or low temperature pathways must be responsible for observed POHC and PIC emissions. We refer to these two pathways as mixing and thermal "failures" of the incinerator, respectively.

In principle, there exists a third failure mode involving reduced residence time or temporal failure. This becomes important for POHCs when the residence time distribution in an incinerator deviates significantly from plug flow (i.e., when some molecules may experience residence times much shorter than the mean residence time). PICs, on the other hand, always experience a sort of temporal failure. Since they are formed at some downstream point in the decomposition sequence, they experience a shorter residence time in the high temperature, free radical rich flame zone than the parent POHC and may only undergo limited decomposition, once formed. For this reason, we sometimes say that a species produced as a PIC may appear more stable than if it were fed to the incinerator as a POHC.

Recently, other researchers have also argued that pyrolysis pathways are responsible for POHC and PIC emissions.[17] Their analysis is based on consideration of the oxidation rate of CO under the apparently oxygen-rich conditions of a typical incinerator. Their results indicate CO levels should be 10 to 10000 times lower than are observed in full-scale incinerators if the nominal oxygen concentration exists at the molecular level throughout the system. This again suggests that oxygen-deficient pathways (i.e., a shortage of OH radicals) exist in the incinerator. This shortage of OH radicals may be magnified in systems containing chlorine. It has been demonstrated that Cl will ultimately result in a reduction in OH through scavenging of hydrogen atoms.[18]

These considerations lead to some important implications concerning the use of CO as a POHC or PIC emissions surrogate. POHCs and PICs may degrade by either pyrolysis or oxidative pathways while CO may only degrade by oxidative reaction with OH. Since we have previously argued that POHC and PIC emissions are primarily due to pyrolysis pathways, this means that *POHC degradation and PIC formation/destruction are occurring in different regions of the incinerator than the reactions responsible for CO formation/destruction*. Thus, it seems unlikely that CO emissions should correlate with POHC or PIC emissions. Some have argued that the destruction of CO is still slower than POHCs or PICs and therefore represents a worst-case scenario, i.e., if CO is low than POHC and PIC emissions must be low. Unfortunately, this argument does not acknowledge the aforementioned reaction kinetic complexities.

It is not surprising that CO emissions did not correlate with POHC or PIC emissions in the TFR. This lack of correlation persisted through upset conditions where benzene and soot emissions were very high, presumably due to the enhancement of pyrolysis pathways that did not involve CO. We strongly suspect that PIC emissions were even higher than measured under low oxygen, upset conditions. Unfortunately, only volatile PICs were analyzed, thus higher molecular weight aromatic and polynuclear aromatic (PAH) PICs were not detectable with our sampling system. Furthermore, many volatile PICs may adsorb onto soot. This would make them difficult to detect even by severe extraction procedures and analysis.[19,20]

We also note that the lack of correlation of CO with trichloroethylene and carbon tetrachloride is more indicative of a lack of correlation of CO with PIC emissions than with POHC destruction efficiency. Laboratory studies have clearly shown that carbon tetrachloride is a high-yield PIC from chloroform and trichloroethylene is produced almost quantitatively from 1,1,2,2-tetrachloroethane.[21] Once again, their formation as PICs seems to be most important under near stoichiometric oxygen, upset conditions which results in poor correlation with CO.

Is this study consistent with other studies which indicate a correlation? Previous studies on a TFR have indicated a double-valued functional relationship between excess air levels and CO emissions.[1,2] The reasons given for this conclusion are as follows. As the excess air level decreases, CO increases because there is insufficient oxygen in the system to react to form OH which can react with CO. At the other extreme, there is so much air introduced to the system, that, even though oxygen is plentiful, the cooling effect of the nitrogen in the air introduced reduces the system temperature below that which is required for the formation of OH. At the minimum of the CO vs. O_2 curve, OH exists in high enough concentration to efficiently oxidize CO to CO_2, resulting in the observed minimum in CO emissions. It is often assumed that this minimum in CO emissions represents the operating conditions most likely to maximize the combustion of hazardous wastes.

Even though these earlier studies seem to offer contradictory conclusions to the study reported on here, there is internal consistancy between all three studies. In the TFR study carried out by La Fond et al.,[1] the effects of suboptimal stoichiometry, poor atomization and flame quenching on emissions of acrylonitrile, benzene, chlorobenzene, and chloroform (diluted to 3.0 percent by mass in No. 2 deisel fuel) were studied. CO emissions increased along with volatile organic emissions for each of three failure modes studied. Different volatile organics exhibited high emissions under different failure modes.

As the stoichiometry varied from less than 100 percent theoretical air to almost 260 percent theoretical air, CO emissions, originally high, decreased and then increased again passing through a minimum of between 120 percent and 140 percent theoretical air. The levels of volatile organic emissions also passed through a similar minimum. Under substoichiometric conditions which resulted in high CO, chloroform exhibited the highest emissions. Under oxidative conditions resulting in high CO, acrylonitrile exhibited the highest emissions. Under extremely high levels of theoretical air in which the CO levels remained elevated, chloroform again exhibited high emissions. When the elevated CO levels were caused in part by poor atomization quality, acrylonitrile had the highest emissions. Under flame quench, it was benzene. Levels of CO emissions did not seem to correlate with the emissions of any one particular organic compound in this study.

Clearly, even in the LaFond study, the volatile organics emitted depended on the means used to create the elevated CO levels. For there to be a useful correlation between CO and organic emissions, elevated CO levels must correspond to elevated volatile organic emissions regardless of whether the CO levels result from suboptimal stoichiometry, poor atomization, flame quench or other upset conditions. That is, whenever CO emissions increase, compound X emissions must increase regardless of the failure mode responsible.

Conclusions

In summary, no correlations were observed between CO emissions and those of any POHCs or PICs in this study. More study is required before the existence of any CO/POHC/PIC correlation can be definitely ruled out. This work must focus on the development of measurement techniques that would enable the detection of a correlation if one exists. This will require the development of a large body of data on which a statistically based search for this correlation can be conducted. Secondly, further study is required to determine whether there is a physical or chemical basis for a correlation between CO and volatile organic emissions. As has been discussed, the chemical reactions responsible for elevated CO emissions may not always be related to the chemical reactions responsible for elevated organic emissions. Quantitative discussions of the degree to which CO reflects hazardous waste incinerator performance must await the results of these additional studies.

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